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Preparation and photophysical properties of halogenated silicon(IV) phthalocyanines substituted axially with poly(ethylene glycol) chains

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Abstract—A series of silicon(IV) phthalocyanines with two axial poly(ethylene glycol) chains $SiPcX_8[(OCH_2CH_2)_nOCH_3]_2$ ($X = H$, Cl, Br; $n \approx 16$) have been prepared of which the photosensitizing properties are enhanced as the periphery of the macrocycle is substituted with heavier halogens. © 2003 Elsevier Science Ltd. All rights reserved.

Being a versatile class of functional dyes, phthalocyanines have been studied extensively for a vast number of practical applications.[1] For those involving the photosensitizing properties of the macrocycles such as photodynamic therapy[2] and photocatalytic degradation of chlorinated phenols,[3] the molecules should exhibit desirable photophysical properties including high triplet (Φ_T) and singlet oxygen quantum yields (Φ_Δ) and long triplet lifetimes (τ_T). Nonaggregated phthalocyanines with a closed-shell metal center such as Zn^{II}, Al^{III} and Si^{IV} are typical candidates for such applications. Although replacing the usual metal center with a heavy metal may increase the intersystem crossing quantum yield (Φ_{isc}) as a result of heavy atom perturbation, the resulting metallophthalocyanines usually have a very short triplet lifetime which cannot trigger the formation of singlet oxygen efficiently.[4] We report herein an alternative strategy to ameliorate the photosensitizing efficiency of phthalocyanines by introducing heavy halogens on the periphery of the ring. Although halogenated phthalocyanines have been known for some time, the use of these heavy substituents to alter the photophysical behavior of phthalocyanines has been little studied.[5] We are particularly interested in silicon(IV) phthalocyanines because of their good photophysical properties and ease of preparation and modification through the manipulation of the axial substituents. To increase the hydrophilicity of the macrocycles and reduce their aggregation tendency, two poly(ethylene glycol) chains have been introduced to the axial positions.[6] It is worth noting that phthalocyanines conjugated with these polymeric materials are well-known for their mesogenic properties.[7] Reports on their photosensitizing applications, however, remain scarce in literature.[8]

The method for preparation of the halogenated phthalocyanines **3b** and **3c** was similar to that for the unsubstituted analogue **3a** (Scheme 1).[9] Starting from dichloro- **1b** or dibromo-phthalonitrile **1c**, bubbling of dry ammonia into a methanol solution in the presence of sodium methoxide led to the corresponding 1,3-diiminoisoindolines **2b** or **2c**, which upon treatment with $SiCl_4$ in quinoline afforded the silicon(IV) phthalocyanines **3b** or **3c**, respectively. Due to the poor solubility of these compounds in common organic solvents, they could only be purified by Soxhlet extraction and characterized with UV–vis spectroscopy.[10] Reactions of **3** (X = H, Cl, Br) with poly(ethylene glycol) methyl ether ($M_n \approx 750$) in the presence of NaH in refluxing toluene resulted in axial substitution giving **4a**–**c** in moderate yields. These polymeric materials have high solubility in many organic solvents and were purified readily by column chromatography. Treatment of diiodophthalonitrile **1d** with ammonia also gave a diiminoisoindoline **2d**, but attempts to prepare the octaiodo counterpart of **4** following the same pathway were not successful. The ^{1}H NMR spectrum of the resulting product gave many signals instead of a singlet in the aromatic region showing that some of the iodo

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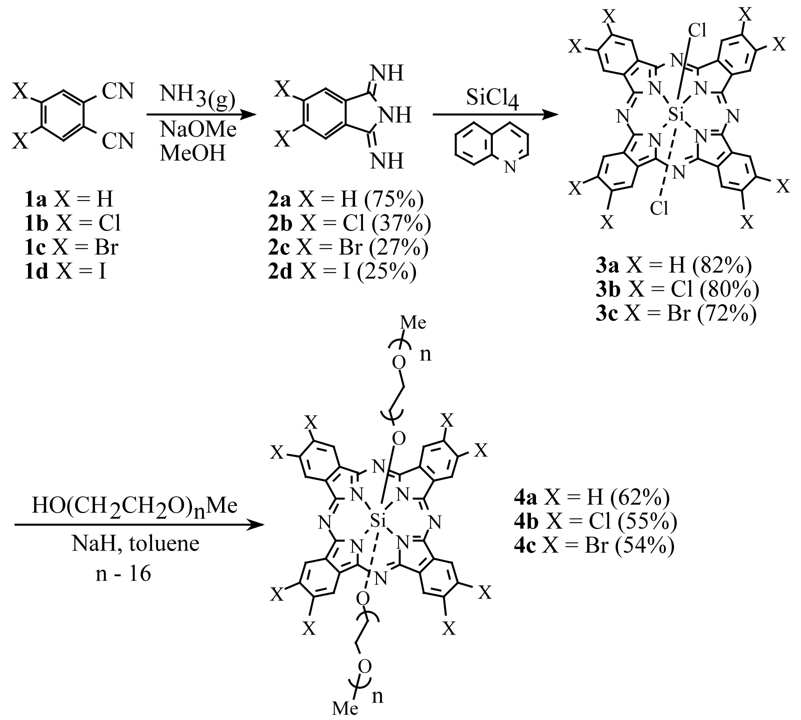

Scheme 1.

groups were replaced under the harsh reaction conditions.

The poly(ethylene glycol)-containing phthalocyanines **4a–c** were unambiguously characterized with various spectroscopic methods.[11] The ^1H NMR spectrum of **4b**, for example, showed an intense aromatic signal at δ 9.64 together with nine well-separated multiplets or virtual triplets centered at δ −1.94, 0.43, 0.88, 1.82, 2.57, 3.06, 3.27, 3.41 and 3.48 assignable to the nine methylene groups nearest to the ring center. These signals, in particular the former ones, were shifted upfield due to the ring current generated by the phthalocyanine ring. The methyl protons resonated at δ 3.37 as a singlet, while signals for the remaining methylene protons overlapped in the region δ 3.54–3.64.

Figure 1 shows the MALDI-TOF mass spectrum of **4a**, which consists of two major envelopes for the molecular ion M^+ and $[M\text{–}O(CH_2CH_2O)_nMe]^+$ species, each separated by 44 mass units, the molecular mass of the repeating unit in poly(ethylene glycol). The distribution of these two envelopes is rather broad leading to a partial overlap. The spectra for the chloro **4b** and bromo **4c** analogues also displayed these two envelopes, but their intensities were much weaker, in particular for **4c**. Signals due to the Na^+ adduct of the $–O(CH_2CH_2O)_nMe$ fragment appeared as the base peaks instead, showing that desorption of these phthalocyanines becomes more difficult upon halogenation.

The electronic absorption and photophysical data of **4a–c** are summarized in Table 1. All the compounds showed typical UV–vis absorptions of nonaggregated phthalocyanines in ethanol with the λ_{max} shifted slightly to the red upon halogenation. The fluorescence emission occurred at 677–688 nm with both the intensity and lifetime decreased along the series X = H>Cl>Br. The intersystem crossing quantum yields (Φ_{isc}) of **4a–c** in toluene were also measured by transient absorption spectroscopy. The value increased steadily from 0.35 to 0.56 along the series, which is in good agreement with the heavy atom effect. Compound **4a**, which is slightly soluble in water, exhibited the Q band absorption at 682 nm and a fluorescence emission at 687 nm in water. It is worth mentioning that due to the strong aggregation effects, fluorescence of phthalocyanines is rarely observed in aqueous media.[12] The chloro **4b** and bromo **4c** analogues have a lower solubility in water. Their absorption spectra showed broad Q bands due to the aggregated species and no fluorescence signal was observed.

One of the key parameters relating to the photosensitizing efficiency is the singlet oxygen quantum yield. The values for these compounds were determined by both steady-state and time-resolved methods giving a consistent result (Table 1).[13] The lifetimes of oxygen luminescence (τ_Δ) were found to be very close (28.3–28.7 ns) for all three compounds in toluene, which provided a further support for the reliability of data. The Φ_Δ values increased from 0.27 to 0.42 and 0.55 as the β-peripheral hydrogen atoms were replaced with chloro and bromo groups, respectively. All these data showed that peripheral substitution of phthalocyanines with heavy halogen atoms reduces the fluorescence emission and promotes the intersystem crossing, leading to a higher singlet oxygen quantum yield. The photosensitizing applications of these compounds are being investigated.

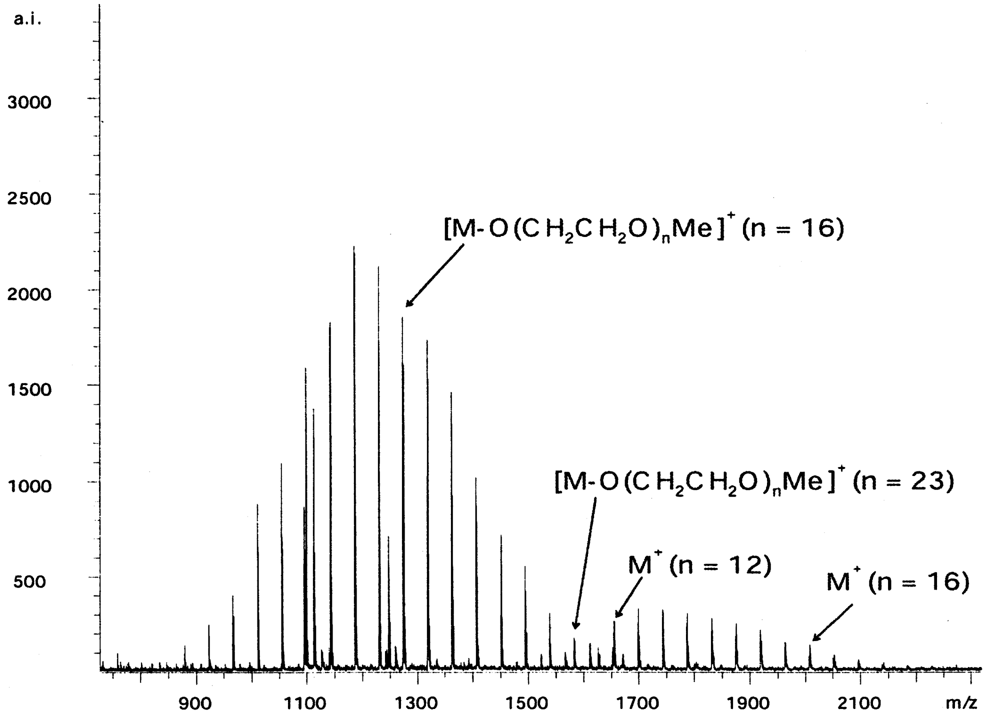

Figure 1.

Table 1. Electronic absorption and photophysical data for **4a**–**c**

Compound	λ_{max} (nm)[a]	λ_{em} (nm)[a]	Relative Φ_F (%)[a]	τ_F (ns)[a]	Φ_{ISC} (%)[b]	Φ_Δ (%)[b,c]
4a	355, 604, 638, 672	677	100	5.4 ± 0.2	35 ± 2	27 ± 5
4b	358, 609, 646, 678	685	75 ± 3	4.6 ± 0.2	44 ± 2	42 ± 5
4c	360, 612, 650, 680	688	45 ± 3	3.3 ± 0.2	56 ± 5	55 ± 5

[a] In ethanol.

[b] In toluene.

[c] Using pheophoride *a* as standard ($\Phi_\Delta = 58\%$).

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10. The UV–vis spectrum of **3b** in pyridine showed a rather broad and weak Q band at 680 nm, while the spectrum of **3c** in pyridine gave typical phthalocyanine absorptions at 362, 614, and 683 nm.
11. Selected spectroscopic data for **4a**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.60–9.64 (m, 8H, Pc-H_α), 8.33–8.36 (m, 8H, Pc-H_β), 3.45–3.64 (m, ca. 104H, CH_2), 3.37 (s, 6H, Me), 3.20 (vt, $J=4.8$ Hz, 4H, CH_2), 2.96 (vt, $J=4.8$ Hz, 4H, CH_2), 2.44 (vt, $J=4.8$ Hz, 4H, CH_2), 1.66 (vt, $J=4.8$ Hz, 4H, CH_2), 0.39 (vt, $J=6.0$ Hz, 4H, CH_2), −1.92 (vt, $J=6.0$ Hz, 4H, CH_2); MS (MALDI-TOF) isotopic clusters peaking at m/z 2010.1 [calcd for M^+ ($n=16$) 2012.0], 1276.2 [calcd for $(M{-}O(CH_2CH_2O)_nMe)^+$ ($n=16$) 1275.6]. **4b**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.64 (s, 8H, Pc-H_α), 3.54–3.64 (m, ca. 92H, CH_2), 3.47–3.49 (m, 4H, CH_2), 3.40–3.42 (m, 4H, CH_2), 3.37 (s, 6H, Me), 3.26–3.28 (m, 4H, CH_2), 3.05–3.07 (m, 4H, CH_2), 2.56–2.58 (m, 4H, CH_2), 1.80–1.83 (m, 4H, CH_2), 0.86–0.90 (m, 4H, CH_2), 0.43 (vt, $J=6.0$ Hz, 4H, CH_2), −1.94 (vt, $J=6.0$ Hz, 4H, CH_2); MS (MALDI-TOF) isotopic clusters peaking at m/z 2295.5 [calcd for M^+ ($n=16$) 2286.7], 1550.7 [calcd for $(M{-}O(CH_2CH_2O)_nMe)^+$ ($n=16$) 1551.2]. **4c**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.83 (s, 8H, Pc-H_α), 3.58–3.64 (m, ca. 92H, CH_2), 3.54–3.56 (m, 4H, CH_2), 3.48–3.50 (m, 4H, CH_2), 3.38 (s, 6H, Me), 3.27–3.29 (m, 4H, CH_2), 3.05–3.07 (m, 4H, CH_2), 2.55–2.57 (m, 4H, CH_2), 1.79–1.81 (m, 4H, CH_2), 0.74–0.78 (m, 4H, CH_2), 0.40 (vt, $J=6.0$ Hz, 4H, CH_2), −1.94 (vt, $J=6.0$ Hz, 4H, CH_2); MS (MALDI-TOF) isotopic clusters peaking at m/z 2666.0 [calcd for $M+Na^+$ ($n=16$) 2665.2], 1904.7 [calcd for $(M{-}O(CH_2CH_2O)_nMe)^+$ ($n=16$) 1906.9].
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